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中国红豆杉枝叶中的紫杉烷二萜

王福生[2]，彭丽艳[1]，赵 昱[1]，古 昆[3]，赵勤实[1*]，孙汉董[1]
（1 中国科学院昆明植物研究所植物化学与西部植物资源持续利用国家重点实验实，云南 昆明 650204；
2 大理学院药学系，云南 大理 671000；3 云南大学化学系，云南 昆明 650091）

摘要：从中国红豆杉（*Taxus chinensis*）枝叶的乙醇提取物中分离得到 8 个紫杉烷二萜，通过波谱分析分别确定为：14β-羟基巴卡亭 VI（1），巴卡亭 VI（2），巴卡亭 IV（3），1β-去羟基巴卡亭 IV（4），云南红豆杉酯甲（5），2α-去乙酰-2α-苯甲酰基-13α-乙酰基云南紫杉亭（6），5α-羟基-2α，7β，9α，10β，13α-五乙酰氧基紫杉-4（20），11-二烯（7）和 Taxacin（8）。其中化合物 1 为新化合物，并报道八个化合物在丙酮中测得的核磁共振信号，化合物 8 的数据属首次报道。

关键词：中国红豆杉；红豆杉科；紫杉烷二萜；14β－羟基巴卡亭 VI
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Taxoids from the Leaves and Stems of *Taxus chinensis*

WANG Fu-Sheng[2]，PENG Li-Yan[1]，ZHAO Yu[1]，GU Kun[3]，
ZHAO Qin-Shi[1*]，SUN Han-Dong[1]
（1 *State Key Laboratory of Phytochemistry and Plant Resources in West China*，*Kunming Institute of Botany*，*Chinese Academy of Sciences*，Kunming 650204，China；2 *Pharmaceutical Department of Dali College*，Dali 671000，China；3 *Department of Chemistry*，*Yunnan University*，Kunming 650091，China）

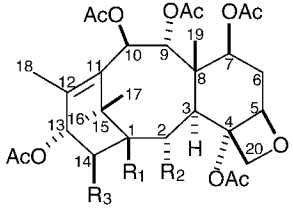
Abstract：A new C－14 oxygenated taxoid，14β-hydroxy-baccatin VI（**1**），together with seven known taxoids，baccatin VI（**2**），baccatin IV（**3**），1β-dehydroxybaccatin IV（**4**），taxayunnasin A（**5**），2α-deacetyl-2α-benzoyl-13α-acetyltaxayuntin（**6**），5α-hydroxy-2α，7β，9α，10β，13α-pentaacetoxy-4（20），11-taxadiene（**7**）and taxacin（**8**）were isolated from the ethanolic extract of leaves and stems of *Taxus chinensis*（Pilg）Rehd. The structures of the compounds were elucidated by spectroscopic techniques. The detailed ^{13}C and ^{1}H NMR data of the seven known compounds were measured in acetone-d_6，and the NMR data of taxacin（**8**）were reported for the first time.

Key words：*Taxus chinensis*；Taxaceae；Taxoids；14β-hydroxy baccatin VI

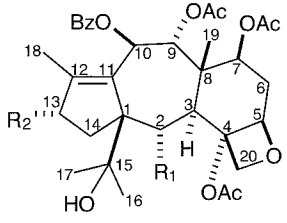
Because of the remarkable antitumor activity，report on the phytochemistry，semisynthesis，biosynthesis，and clinic use of paclitaxel and related taxoids have proliferated，and the progressing of them have been published a lot of articles（Baloglu *et al*，1999；Kingston，2000）. Although paclita-

* To whom correspondence should be addressed. Phone（86）8715223254. Fax：（86）8715216343.
E－mail：qinshizhao@hotmail. com
Received date：2003－04－14，Accepted date：2003－04－24
作者简介：王福生（1965－）男，在职硕士研究生，主要从事天然药物化学研究。

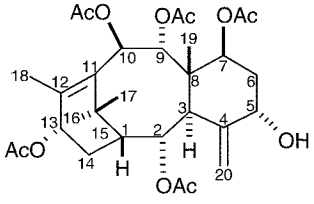
xel and its semisynthetic analogue have exhibited significant clinical curative effect, however, these drugs often result in a number of side effects and multidrug resistances (MDR) (Ojima *et al*, 1997). Thus, it is essential to develop the new generation of anticancer medicines, which would be possessed of superior antitumor activity and fewer side effects. In the last twenty years, many phytochemists have been devoted to isolated new taxoids and have isolated a number of new taxoids from various *Taxus species* (Li *et al*, 2002; Shinozaki *et al*, 2002; Banskota *et al*, 2002; Shen *et al*, 2002). *Taxus chinensis* (Pilg) Rehd, indigenous to China, is considered as a promising source of taxane-type diterpenoids (Zhang *et al*, 1991; Li *et al*, 1993; Tanaka *et al*, 1994). In the continuation of our research aim at new taxoids, we have further investigated on the chemical constituents of *Taxus chinensis* (Pilg) Rehd collected in Sichuan Province. As a result, a new C – 14 oxygenated taxoid, 14β-hydroxy-baccatin VI (**1**), together with seven known taxoids, baccatin VI (**2**), baccatin IV (**3**), 1β-dehydroxybaccatin IV (**4**), taxayunansin A (**5**), 2α-deacetyl-2α-benzoyl-13α-acetyltaxayuntin (**6**), 5α-hydroxy-2α, 7β, 9α, 10β, 13α-pentaacetoxy-4 (20), 11-taxadiene (**7**) and taxacin (**8**) were isolated from the ethanolic extract of the leaves and stems. The structures of the compounds were elucidated by spectroscopic techniques.



1 R_1=OH; R_2=OBz; R_3=OH
2 R_1=OH; R_2=OBz; R_3=H
3 R_1=OH; R_2=OAc; R_3=H
4 R_1=H; R_2=OAc; R_3=H



5 R_1=OAc; R_2=OH
6 R_1=OBz; R_2=OAc



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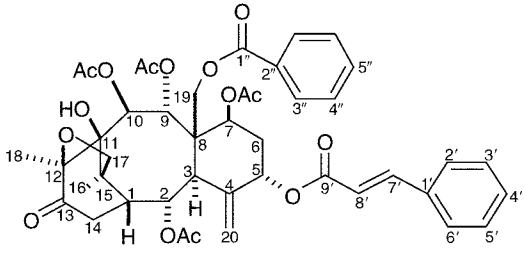

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Results and Discussion

Compound (**1**), obtained as colorless needle crystals with $[\alpha]_D^{15.8}$ + 9.42 (*c* 0.57, MeOH), was determined to have formula $C_{37}H_{46}O_{15}$ by positive HRFABMS (*m/z* 731.2911 $[M+H]^+$, calcd 731.2915). The ^{13}C and DEPT NMR spectra of **1** showed 37 carbon signals which were composed of

six ester carbonyl carbons, two olefinic carbons, six aromatic ring carbons, four methyl carbons, two methylene carbons, eight methine (including seven oxygenated methine) carbons, four quaternary carbons (including two oxygenated), and five acetyl methyl carbons, which suggested **1** had a taxoid basic skeleton, combined with the consideration of the structure of taxoids previously isolated from the genus *Taxus* plant. Furthermore, compound **1** was suggested to have a skeleton of 6/8/6 ring-system taxoid with oxetane ring deduced from the characteristic NMR signals at δ 76.8 (s, C-1), 47.4 (d, C-3), 46.6 (s, C-8), 136.6 (s, C-11), 138.7 (s, C-12), 43.6 (s, C-15), while the three signals at δ 82.0 (C-4), 84.2 (C-5), and 76.4 (C-20) corresponding to the three carbons signals of oxetane ring.

Table 1　NMR data of the compounds **1** and **2**[a]

Position	1		HMBC	2	
	δ_C	δ_H		δ_C	δ_H
1	76.8 s		H-2, 3, 14, 16, 17, OH	78.2 s	
2	73.3 d	6.03 (1H, d, 6.1)	H-3, 14	73.9 d	5.92 (1H, d, 6.0)
3	47.4 d	3.18 (1H, d, 6.1)	H-2, 5, 20α, 20β	48.0 d	3.24 (1H, d, 6.0)
4	82.0 s		H-3, 5, 6α, 6β, 20α	82.0 s	
5	84.2 d	4.92 (1H, d, 8.9)	H-3, 6α, 6β, 20β	84.2 d	4.94 (1H, d, 7.9)
6	35.4 t	2.41 (1H, m)	H-7	35.3 t	2.46 (1H, m)
		1.79 (1H, m)			1.84 (1H, m)
7	72.5 d	5.56 (1H, dd, 9.8, 8.0)	H-3, 5, 6α, 6β, 9, 19	72.5 d	5.53 (1H, dd, 9.7, 7.8)
8	46.6 s		H-2, 3, 7, 9, 19	46.5 s	
9	75.4 d	6.14 (1H, brs)[b]	H-3, 7, 10, 19	75.4 d	5.97 (1H, d, 11.3)
10	71.3 d	6.14 (1H, brs)[b]	H-9	71.2 d	6.17 (1H, d, 11.3)
11	136.6 s		H-9, 10, 13, 16, 17, 18	139.6 s	
12	138.7 s		H-10, 13, 18	141.3 s	
13	79.2 d	6.07 (1H, brd, 6.7)	H-14	70.2 d	6.14 (1H, t, 8.7)
14	70.7 d	4.28 (1H, d, 6.4)	H-2, 13, OH-14	36.8 t	2.37 (2H, m)
		4.41 (1H, s, OH-14)			
15	43.6 s		H-10, 14, 2, 16, 17	43.8 s	
16	28.7 q	1.17 (3H, s)	H-17	28.4 q	1.20 (3H, s)
17	24.5 q	1.74 (3H, s)	H-16	23.4 q	1.75 (3H, s)
18	14.5 q	1.98 (3H, s)		15.2 q	1.98 (3H, d, 1.0)
19	13.0 q	1.62 (3H, s)	H-3, 7, 9	13.1 q	1.60 (3H, s)
20	76.4 t	4.17 (1H, d, 8.0)	H-3	76.6 t	4.18 (1H, d, 7.9)
		4.12 (1H, d, 8.0)			4.07 (1H, d, 7.9)
OCOPh	166.1 s		H-2, 2′, 6′	166.3 s	
i	131.0 s		H-2′, 3′, 6′	130.7 s	
o	130.7 d	8.11 (2H, d, 8.3)	H-3′, 4′, 5′	131.0 d	8.09 (2H, dd, 8.5, 1.4)
m	129.4 d	7.51 (2H, t, 7.8)	H-2′, 4′, 5′	129.3 d	7.52 (2H, dd, 8.5, 7.4)
p	134.1 d	7.63 (1H, t, 7.4)	H-2′, 3′, 5′, 6′	134.1 d	7.62 (1H, t, 7.4)
OAc	171.3 s			171.1 s	
OAc	170.9 s		H-13, -$COCH_3$	170.8 s	
OAc	170.8 s		H-9, -$COCH_3$	170.3 s	
OAc	170.3 s		H-7, -$COCH_3$	170.2 s	
OAc	169.4 s		H-10, -$COCH_3$	169.4 s	
OAc	22.8 q	2.37 (3H, s)		22.9 q	2.31 (3H, s)
OAc	21.4 q	2.21 (3H, s)		21.4 q	2.18 (3H, s)
OAc	21.1 q	2.13 (3H, s)		21.2 q	2.11 (3H, s)
OAc	20.8 q	2.08 (3H, s)		20.9 q	2.06 (3H, s)
OAc	20.8 q	1.98 (3H, s)		20.8 q	1.96 (3H, s)

[a] ^{13}C, ^1H NMR and HMBC spectra were measured at 100, 400 and 500 MHz, respectively, in acetone-d_6 (δ in ppm, J in Hz). [b] H-9 and H-10 appeared as broad singlet in acetone-d_6, while they appeared as 6.60 (1H, d, 11.2, H-9); 6.67 (1H, d, 11.2, H-10) in C_5D_5N.

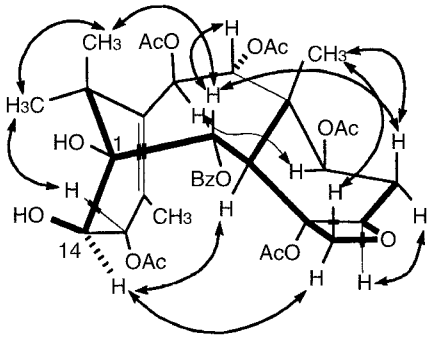

Fig. 1 Key NOESY correlations for **1**

Comparison of the ^{13}C and ^{1}H NMR spectra (Table 1) of **1** with that of baccatin VI (**2**), a known taxoid isolated from the same plant this time, revealed that the methylene signals [δ_C 36.8 (t, C – 14) and δ_H 2.37 (2H, m, H_2 – 14)] in **2** were replaced by the methine signals [δ_C 70.7 (t, C – 14) and δ_H 4.28 (1H, d, 6.4, H – 14)] in **1**, which was approved by the ^{1}H – ^{1}H COSY correlations of a methine proton (δ_H 4.28, H – 14) with another methine proton (δ_H 6.07, H – 13), and by the HMBC correlations of the proton signal (H – 14) with carbon signals [δ_C 76.8 (C – 1), 73.3 (C – 2), 79.2 (C – 13), 43.6 (C – 15)]. Therefore, compound **1** differed from baccatin VI (**2**) by the presence of a hydroxyl group at C – 14 in **1**, which was further confirmed by the HMBC correlation of a hydroxyl proton signal (δ_H 4.41, s, OH – 14) with the signal of C – 14. Finally, the relative stereochemistry of **1** was established by its NOESY spectrum (Figure 1). The protons H – 14/H – 3 and H – 14/H – 20α showed correlations with each other, which indicated H – 14 has α orientation. On the basis of the spectral evidence described above, the structure of **1** was established as 14β-hydroxy baccatin VI.

The seven known compounds were identified as baccatin VI (**2**) (Senilh *et al*, 1984; Della Casa de Marcano *et al*, 1975), baccatin IV (**3**) (Della Casa de Marcano *et al*, 1975), 1β-dehydroxybaccatin IV (**4**) (Della Casa de Marcano *et al*, 1975), taxayunnasin A (**5**) (Liu *et al*, 1992), 2α-deacetyl-2α-benzoyl-13α-acetyl taxayuntin (**6**) (Chen *et al*, 1993), 5α-hydroxy-2α, 7β, 9α, 10β, 13α-pentaacetoxy-4 (20), 11-taxadiene (**7**) (Kingston *et al*, 1982) and taxacin (**8**) (Yoshizaki *et al*, 1988). The structures of the known compounds were elucidated by spectroscopic techniques and confirmed by comparison of spectral data with literature report.

Experimental

General The Melting point was determined on an XRC – 1 micro melting point apparatus and uncorrected. NMR spectra were performed on a Bruker AM – 400 MHz and DRX – 500 MHz spectrometer. FABMS and HRFABMS were taken on a VG Auto Spec – 3000 or on a Finnigan MAT 90 instrument. IR spectra were recorded on a Bio-Rad FTS – 135 spectrometer with KBr pellets. UV spectrum was obtained on a UV 2401 PC spectrometer. Optical rotations were measured with a HORIBA SEPA – 300 High Sensitive Polarimeter. Column chromatography was performed either on 200 – 300 mesh silica gel and 10 – 40 μm silica gel H; 43 – 63 μm Lichroprep RP – 18 and Sephadex LH – 20 were used for column chromatography. Fractions were monitored by TLC and spots were visualized by heating silica gel plates sprayed with 10% H_2SO_4 in EtOH.

Plant material The leaves and stems of *Taxus chinensis* (Pilg) Rehd were collected in Sichuan Province. A voucher specimen has been deposited at the Yunnan Academy of Forestry, Kunming, Yunnan, People's Republic of China.

Extraction and isolation The dried plant material (15 kg) was extracted three times with 95% ethanol to yield a

crude extract. After evaporation of the solvent, the residue was dissolved with MeOH/H_2O (9:1), and the MeOH-soluble part was further reextracted with chloroform to give the extract. The chloroform extract was chromatographed on Silica gel columns using solvents of increasing polarity (petroleum-EtOAc, 9:1 – 2:8, acetone, v/v) to give ten fractions, and three of these fractions (4 – 6, 16.65 g) was further isolated by repeated column chromatography on silica gel to give baccatin VI (0.2 g), baccatin IV (0.4 g), 1β-dehydroxybaccatin IV (20 mg), and taxayunnansin A (1.0 g), 1β-dehydroxy baccatin IV (15 mg), 14β-hydroxy baccatin VI (16 mg), taxacin (12 mg) and 5α-hydroxy-2α, 7β, 9α, 10β, 13α-pentaacetoxy-4 (20), 11-taxadiene (95 mg).

14β-hydroxy baccatin VI (1), $C_{37}H_{46}O_{15}$, colorless needle crystals (acetone), mp 241 – 243℃, $[\alpha]_D^{15.8}$ + 9.42 (*c* 0.57, MeOH). UV λ_{max}^{MeOH} (log ε) 228.4 (4.22), 200.2 (3.84), 274.4 (2.94) nm. IR ν_{max}^{KBr} 3443 (OH), 1740 (ester C=O), 1636, 1437, 1374, 1250, 1106, 713 cm^{-1}. ^1H and ^{13}C NMR see table **1**. Positive FABMS *m/z* (%): 731 ($[M+H]^+$, 32), 713 (53), 671 (100), 447 (13), 105 (49), 83 (37); positive HRFABMS *m/z* 731.2911 $[M+H]^+$ (calcd for $C_{37}H_{47}O_{15}$, 731.2915).

Baccatin VI (2), $C_{37}H_{46}O_{14}$, white powder, positive FABMS *m/z* (%): 715 ($[M+H]^+$, 25), 655 (100), 553 (10), 371 (6), 311 (3). $[\alpha]_D^{27.1}$ – 10.93 (*c* 1.04, acetone). ^1H and ^{13}C NMR see table **1**.

Baccatin IV (3), $C_{32}H_{44}O_{14}$, white powder, positive FABMS *m/z* (%): 653 ($[M+H]^+$, 18), 593 (100), 533 (13), 491 (11), 371 (6). ^{13}C NMR (100 MHz, acetone-d_6): δ 77.7 (s, C – 1), 70.2 (d, C – 2), 47.9 (d, C – 3), 81.8 (s, C – 4), 84.3 (d, C – 5), 35.3 (t, C – 6), 72.5 (d, C – 7), 46.4 (s, C – 8), 73.3 (d, C – 9), 71.3 (d, C – 10), 135.0 (s, C – 11), 141.3 (s, C – 12), 75.6 (d, C – 13), 36.9 (t, C – 14), 43.7 (s, C – 15), 28.4 (q, C – 16), 23.2 (q, C – 17), 15.1 (q, C – 18), 13.1 (q, C – 19), 76.6 (t, C – 20); OAc: 171.1 (2C, s), 170.8 (s), 170.4 (s), 170.2 (s), 169.4 (s), 23.0 (q), 21.4 (q), 21.2 (q), 20.8 (3C, q). ^1H NMR (400 MHz acetone-d_6): δ 5.65 (1H, d, 5.7, H – 2), 3.01 (1H, d, 5.7, H – 3), 4.92 (1H, d, 8.1, H – 5), 1.73 (1H, m, H – 6α), 2.40 (1H, m, H – 6β), 5.48 (1H, dd, 9.7, 7.8, H – 7), 6.00 (1H, d, 11.3, H – 9), 6.08 (1H, d, 11.3, H – 10), 6.09 (1H, m, H – 13), 2.18 (2H, overlap, H_2 – 14), 1.17 (3H, s, Me – 16), 1.66 (3H, s, Me – 17), 1.94 (3H, s, Me – 18), 1.53 (3H, s, Me – 19), 4.47 (1H, d, 7.8, H – 20α), 4.14 (1H, d, 7.8, H – 20β), OAc: 2.19 (3H, s), 2.14 (3H, s), 2.09 (3H, s), 2.08 (3H, s), 2.01 (3H, s), 1.98 (3H, s).

1β-dehydroxybaccatin IV (4), $C_{32}H_{44}O_{13}$, colorless prisms, positive FABMS *m/z* (%): 637 ($[M+H]^+$, 19), 577 (100), 517 (2), 475 (9). ^{13}C NMR (100 MHz, acetone-d_6): δ 45.2 (d, C – 1), 69.4 (d, C – 2), 47.7 (d, C – 3), 81.5 (s, C – 4), 84.0 (d, C – 5), 35.5 (t, C – 6), 71.6 (d, C – 7), 46.3 (s, C – 8), 72.7 (d, C – 9), 71.2 (d, C – 10), 134.2 (s, C – 11), 139.4 (s, C – 12), 75.7 (d, C – 13), 26.9 (t, C – 14), 38.7 (s, C – 15), 31.4 (q, C – 16), 27.4 (q, C – 17), 15.1 (q, C – 18), 13.1 (q, C – 19), 77.0 (t, C – 20); OAc: 171.1 (s), 170.9 (s), 170.3 (s), 170.2 (s), 170.0 (s), 169.3 (s), 22.9 (q), 21.4 (2C, q), 21.2 (q), 20.8 (2C, q). ^1H NMR (400 MHz acetone-d_6): δ 2.89 (1H, d, 5.8, H – 1), 5.60 (1H, dd, 5.8, 2.2, H – 2), 3.2 (1H, d, 5.4, H – 3), 4.98 (1H, d, 9.0, H – 5), 2.43 (1H, m, H – 6α), 1.80 (1H, m, H – 6β), 5.55 (1H, dd, 9.8, 7.8, H – 7), 5.95 (1H, d, 11.3, H – 9), 6.10 (1H, d, 11.3, H – 10), 5.92 (1H, dd, 2.9, 1.5, H – 13), 1.67 (1H, m, H – 14a), 2.48 (1H, m, H – 14b), 1.78 (3H, s, Me – 16), 1.13 (3H, s, Me – 17), 1.99 (3H, s, Me – 18), 1.55 (3H, s, Me – 19), 4.52 (1H, d, 8.1, H – 20α), 4.20 (1H, d, 8.1, H – 20β); OAc: 2.23 (3H, s), 2.18 (3H, s), 2.12 (3H, s), 2.07 (3H, s), 2.03 (3H, s), 1.97 (3H, s).

Taxayunnansin A (5), $C_{35}H_{44}O_{13}$, colorless prism. ^{13}C NMR (100 MHz, acetone-d_6): δ 68.1 (s, C – 1), 71.4 (d, C – 2), 45.4 (d, C – 3), 79.4 (s, C – 4), 82.2 (d, C – 5), 35.7 (t, C – 6), 69.9 (d, C – 7),

44.3 (s, C-8), 76.7 (d, C-9), 77.6 (d, C-10), 134.5 (s, C-11), 152.5 (s, C-12), 68.8 (d, C-13), 39.9 (t, C-14), 76.0 (s, C-15), 26.6 (q, C-16), 28.3 (q, C-17), 12.0 (q, C-18), 12.9 (q, C-19), 74.8 (t, C-20); 10-OBz: 165.0 (s), 130.8 (s), 130.2 (2C, d), 129.5 (2C, d), 134.1 (d); OAc: 171.5 (s), 170.5 (s), 170.3 (s), 169.9 (s), 22.1 (q), 21.8 (q), 21.4 (q), 20.8 (q). ^{1}H NMR (400 MHz acetone-d_6): δ 6.18 (1H, d, 7.8, H-2), 3.08 (1H, d, 7.8, H-3), 4.95 (1H, d, 8.5, H-5), 1.78 (1H, dd, 14.9, 7.8, H-6α), 1.73 (1H, d, 6.6, H-6β), 5.55 (1H, t, 8.5, H-7), 6.24 (1H, d, 10.6, H-9), 6.41 (1H, d, 10.6, H-10), 4.56 (1H, t, 6.8, H-13), 2.50 (1H, dd, 15.1, 8.6, H-14), 2.26 (1H, dd, 14.6, 7.3, H-14), 1.18 (3H, s, Me-16), 1.65 (3H, s, Me-17), 1.71 (3H, s, Me-18), 1.14 (3H, s, Me-19), 4.53 (1H, d, 7.3, H-20α), 4.18 (1H, d, 7.3, H-20β); 10-OBz: 7.89 (2H, d, 8.6, H-2′, 6′), 7.47 (2H, t, 7.6, H-3′, 5′), 7.58 (1H, t, 7.6, H-5′); OAc: 2.15 (3H, s), 2.12 (3H, s), 2.11 (3H, s), 2.02 (3H, s).

2α-deacetyl-2α-benzoyl-13α-acetyltaxayuntin (6), $C_{42}H_{48}O_{14}$, amorphous powder, positive FABMS *m/z* (%): 777 ([M+H]$^+$, 15), 655 (100), 537 (8). ^{13}C NMR (100 MHz, acetone-d_6): δ 68.8 (s, C-1), 69.1 (d, C-2), 45.7 (d, C-3), 79.6 (s, C-4), 85.0 (d, C-5), 35.7 (t, C-6), 71.3 (d, C-7), 44.3 (s, C-8), 77.3 (d, C-9), 68.9 (d, C-10), 137.6 (s, C-11), 148.1 (s, C-12), 79.1 (d, C-13), 37.2 (t, C-14), 75.8 (s, C-15), 27.0 (q, C-16), 28.2 (q, C-17), 12.0 (q, C-18), 13.0 (q, C-19), 74.8 (t, C-20); 10-OBz: 165.1 (s), 130.5 (s), 130.3 (2C, d), 129.5 (2C, d), 134.1 (d); 2-OBz: 166.8 (s), 130.7 (s), 130.5 (2C, d), 129.6 (2C, d), 134.4 (d); OAc: 170.9 (s), 170.3 (s), 170.2 (s), 170.0 (s), 22.2 (q), 21.4 (q), 21.1 (q), 20.8 (q). ^{1}H NMR (400 MHz, acetone-d_6): δ 6.52 (1H, d, 7.8, H-2), 3.17 (1H, d, 7.8, H-3), 4.97 (1H, d, 8.1, H-5), 2.51 (1H, t, 8.6, H-6α), 1.78 (1H, t, 8.8, H-6β), 5.60 (1H, t, 8.5, H-7), 6.24 (1H, d, 10.6, H-9), 6.41 (1H, d, 10.6, H-10), 5.70 (1H, t, 7.5, H-13), 2.01 (1H, overlap, H-14α), 2.57 (1H, m, H-14β), 1.12 (3H, s, Me-16), 1.23 (3H, s, Me-17), 1.87 (3H, s, Me-18), 1.72 (3H, s, Me-19), 4.37 (1H, d, 7.7, H-20α), 4.01 (1H, d, 7.5, H-20β), 10-OBz: 8.09 (2H, d, 8.4), 7.49 (2H, t, 7.9), 7.57 (1H, t, 7.9); 2-OBz: 7.93 (2H, d, 8.4), 7.47 (2H, t, 7.9), 7.55 (1H, t, 7.9), OAc: 2.27 (3H, s), 2.12 (3H, s), 2.06 (3H, s), 1.73 (3H, s).

5α-hydroxy-2α, 7β, 9α, 10β, 13α-pentaacetoxy-4 (20), 11-taxadiene (7), $C_{30}H_{42}O_{11}$, colourless prism, EIMS (70 eV) m/z (%): 578 [M]$^+$ (51), 560 (40), 518 (27), 458 (47), 416 (53), 398 (62), 374 (29), 356 (72), 338 (74), 314 (34), 297 (48), 278 (100), 263 (69), 235 (43), 209 (29), 163 (40), 145 (52), 133 (70), 121 (48), 105 (42), 91 (32), 60 (30). ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.1 (d, C-1), 69.5 (d, C-2), 40.6 (d, C-3), 144.7 (s, C-4), 75.3 (d, C-5), 37.1 (t, C-6), 69.5 (d, C-7), 47.8 (s, C-8), 75.8 (d, C-9), 71.9 (d, C-10), 133.9 (s, C-11), 138.3 (s, C-12), 70.3 (d, C-13), 28.6 (t, C-14), 37.2 (s, C-15), 26.0 (q, C-16), 32.0 (q, C-17), 15.9 (q, C-18), 12.9 (q, C-19), 116.6 (t, C-20); OAc: 170.1 (s), 169.8 (s), 169.6 (s), 169.3 (s), 169.2 (s), 21.5 (q), 21.4 (q), 21.4 (q), 21.0 (q), 20.8 (q). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.85 (1H, d, 9.2, H-1), 5.49 (1H, dd, 6.2, 1.8, H-2), 3.47 (1H, d, 6.0, H-3), 4.23 (1H, t, 2.8, H-5), 2.18 (1H, m, H-6a), 1.45 (1H, dd, 15.8, 5.4, H-6b), 5.60 (1H, dd, 10.7, 5.2, H-7), 5.84 (1H, d, 10.9, H-9), 6.20 (1H, d, 10.9, H-10), 5.75 (1H, m, H-13), 2.62 (1H, m, H-14α), 1.57 (1H, m, H-14β), 1.69 (3H, s, Me-16), 1.00 (3H, s, Me-17), 2.21 (3H, s, Me-18), 0.93 (3H, s, Me-19), 4.83 (1H, brs, H-20a), 5.27 (1H, brs H-20b), OAc: 2.09 (3H, s); 2.02 (6H, s), 1.99 (3H, s), 1.94 (3H, s).

Taxacin (8), $C_{44}H_{48}O_{15}$, colourless lameller, positive FABMS m/z (%): 817 ([M + H]$^+$, 9), 669 (100), 609 (21), 549 (4), 105 (100). ^{13}C NMR (100 MHz, acetone-d_6): δ 48.7 (s, C-1), 70.8 (d, C-2), 41.4 (d, C-3), 141.8 (s, C-4), 75.2 (d, C-5), 37.0 (t, C-6), 69.5 (d, C-7), 50.2 (s, C-8), 69.8 (d, C-9), 64.9 (d, C-10), 81.4 (s, C-11), 92.1 (s, C-12), 205.1 (s, C-13), 34.7 (t, C-14), 50.0 (s, C-15), 16.1 (q, C-16), 82.3 (t, C-17), 12.9 (q, C-18), 62.2 (t, C-19), 116.1 (t, C-20); 19-OBz: 167.1 (s), 130.6 (s), 130.7 (2C, d), 129.3 (2C, d), 134.1 (d); 5-OCinnamoyl: 165.1 (s), 131.1 (d), 146.1 (d), 135.8 (s), 130.9 (2C, d), 129.6 (2C, d), 131.1 (d); OAc: 171.6 (s), 170.1 (s), 169.3 (s), 168.9 (s), 21.3 (q), 21.2 (q), 20.9 (q), 20.8 (q). ^{1}H NMR (400 MHz acetone-d_6): δ 2.68 (1H, m, H-1), 6.24 (1H, dd, 10.4, 2.8, H-2), 3.18 (1H, d, 10.2, H-3), 5.53 (1H, dd, 6.2, 2.7, H-5), 2.26 (1H, ddd, 2.3, 6.4, 14.7, H-6α), 1.84 (1H, m, H-6β), 5.56 (1H, t, 6.5, H-7), 5.67 (1H, d, 2.8, H-9), 5.39 (1H, d, 2.8, H-10), 2.56 (1H, d, 19.9, H-14α), 3.11 (1H, dd, 11.9, 19.2, H-14β), 1.35 (3H, s, Me-16), 3.96 (1H, d, 7.9, H-17a), 3.66 (1H, d, 7.9, H-17b), 1.12 (3H, s, Me-18), 5.00 (1H, d, 12.3, H-19a), 4.49 (1H, d, 12.3, H-19b), 5.60 (1H, s, H-20a), 4.82 (1H, s, H-20b); 19-OBz: 8.21 (2H, dd, 6.3, 8.2, H-3″), 7.42 (2H, t, 7.4, H-3′, 5′), 7.66 (1H, t, 8.6, H-5″); 5-OCinnamoyl: 7.92 (2H, t, 8.9, H-2′, 6′), 7.42 (2H, t, 7.4, H-3′, 5′), 7.47 (1H, m, H-4′), 7.96 (1H, d, 16.2, H-7′), 6.77 (1H, d, 16.2, H-8′); OAc: 2.10 (3H, s); 2.07 (3H, s); 2.03 (3H, s); 1.92 (3H, s).

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